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## APPLICATION OF FOAM SEPARATION TO AQUEOUS SOLUTIONS OF TRINITROTOLUENE (TNT) PART II, REMOVAL OF ORGANIC EXPLOSIVES WITH SURFACTANTS

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20. ABSTRACT (Continued)

surfactant. Nitroguanidine is unaffected by the surfactant treatment, but can be destroyed by contact with an ion exchange resin.

The methods of analysis are described for RDX and TNT in pink water and for nitroglycerin and nitroguanidine in other wastewaters. The recommended process for pilot plant operation is also described.

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## INTRODUCTION

Previous investigations (reference 1) have shown that certain surfactants containing amino groups react rapidly with TNT in aqueous solution. A dark brown TNT surfactant complex precipitates and can be separated from the solution by filtration. This process quantitatively removes the TNT from aqueous solution. However, the applicability of the surfactant process to removing TNT and RDX from Composition B wastewater, as well as other wastewaters containing dissolved organic explosives such as nitroguanidine and nitroglycerin, was investigated.

## PROCEDURES AND RESULTS

### Optimum Conditions for Removal of TNT with N-Tallow-1,3-Diaminopropane

TNT can be removed quantitatively, with 48 hrs reaction time at ambient temperature, using N-tallow-1,3-diaminopropane, a surfactant, when the molar ratio of the surfactant to TNT is 3:1. Various experiments were conducted to establish the optimum conditions for the removal of TNT within a more reasonable time, i.e., 3-5 hrs. The initial concentration of TNT in pink water was 139 ppm; the concentration of stock surfactant solution was 10.0 mg/L. The stock solution of the surfactant was prepared by dissolving the surfactant in a dilute HCl solution. Varying amounts of the surfactant were added to the TNT solutions. Each solution was mixed well and its pH adjusted to  $10.5 \pm 0.5$  with NaOH. The solutions were stirred at room temperature. Samples were filtered periodically and the TNT content of the filtrate was determined.

The optimum conditions for removal of TNT (initial concentration 139 mg/L) with N-tallow-1,3-diaminopropane are: pH =  $10.5 \pm 0.5$  and 600 to 700 mg/L surfactant (the molar ratio of TNT to surfactant was 1:2.6 - 3.2). The results are summarized in Tables 1 and 2.

Table 1. Removal of TNT from aqueous solution  
using n-tallow-1,3-diaminopropane, 600 mg/L

<u>TNT left in solution (mg/L)</u>				
<u>Initial pH</u>	<u>Initial</u>	<u>2 hrs.</u>	<u>3 hrs.</u>	<u>4 hrs.</u>
10.35	139	1.02	0.80	0.60
10.71	139	1.4	0.86	0.80
10.95	139	2.92	2.22	1.99

Table 2. Removal of TNT from aqueous solution  
using n-tallow-1,3-diaminopropane, 700 mg/L

<u>TNT left in solution (mg/L)</u>				
<u>Initial pH</u>	<u>Initial</u>	<u>2 hrs.</u>	<u>3 hrs.</u>	<u>4 hrs.</u>
10.60	139	3.40	1.30	1.03
10.37	139	2.0	0.90	0.8
10.82	139	3.0	1.9	1.8

The best molar ratio for the quantitative removal of TNT is 1:3 (TNT to surfactant). The effects of varying the concentration of surfactant are summarized in table 3.

Table 3. Effect of surfactant concentration  
on TNT removal

Initial Concentration (mg/L)    TNT left in solution, (mg/L)

<u>Surfactant</u>	<u>TNT</u>	<u>Initial pH</u>	<u>1-½ hrs.</u>	<u>3 hrs.</u>	<u>4 hrs.</u>
200 <sup>a</sup>	139	10.48	40.1	33.0	30.0
400	139	10.53	15.0	9.0	7.7
480	139	10.43	4.7	3.0	2.0
560	139	10.78	6.4	1.7	1.3
600 <sup>b</sup>	139	10.47	4.3	1.3	0.9
700 <sup>c</sup>	139	10.37	4.0	0.9	0.8
800 <sup>d</sup>	139	10.43	4.0	1.5	0.9

Molar ratio of TNT to surfactant is <sup>a</sup>1:0.85, <sup>b</sup>1:2.6,  
<sup>c</sup>1:3.2, <sup>d</sup>1:3.5

#### Optimum Conditions for Removal of TNT with Quaternary Ammonium Surfactant

When equal molar ratios of TNT, propylenediamine, and surfactant (hexadecyltrimethylammonium bromide) were reacted in aqueous solution, TNT was removed quantitatively (ref 1). However, this study showed that the amount of TNT removed was very sensitive to the concentrations of the surfactant and amine used. When the pH of the solution was adjusted to  $10.5 \pm 0.5$  with NaOH or HCl, the TNT was quantitatively removed by using certain quaternary ammonium surfactants.

#### Removal of TNT using Hyamine 3500

Hyamine 3500 (Rohm and Haas Co) is a blend of n-alkyl (50% C<sub>14</sub>, 40% C<sub>12</sub>, 10% C<sub>16</sub>) dimethylbenzylammonium chloride. The average molecular weight of the active ingredient is 350.6. Two forms of Hyamine 3500 are available: a 50% aqueous solution (\$.75/lb), and an 80% ethanol solution

(\$1.17/lb). One liter solutions containing varying amounts of Hyamine 3500 (80% concentration) were prepared; the pH of each was adjusted to  $10.5 \pm 0.5$  with NaOH or HCl. The solutions were stirred at ambient temperature. Samples were taken periodically and were filtered. The TNT content in each filtrate was determined. The results are summarized in tables 4 and 5.

Table 4. Effects of surfactant concentration on the removal of TNT using Hyamine 3500

Surfactant used (mg <sup>a</sup> )	pH		TNT left in solution (mg/L)			
	Initial	After 5 hrs.	Initial	3 hrs.	4 hrs.	5 hrs.
74.3	10.68	10.48	139	43.7	43.2	43.1
148.6	10.77	10.56	139	11.1	8.4	7.6
222.9 <sup>b</sup>	10.81	10.64	139	0.94	0.90	0.73
297.2 <sup>c</sup>	10.64	10.41	139	0.6	0.4	0.3
445.8	10.52	10.13	139	2.4	2.3	1.9
594.4	No precipitation was obtained					

<sup>a</sup>Measured as active ingredient

<sup>b</sup>The molar ratio of surfactant and TNT was 1.04:1

<sup>c</sup>The molar ratio of surfactant and TNT was 1.4:1

Table 5. Effect of pH on the removal of TNT using Hyamine 3500\*

pH		TNT left in Solution, (mg/L)			
Initial	After 5 hrs.	Initial	3 hrs.	4 hrs.	5 hrs.
10.26	10.15	139	2.44	2.10	1.84
10.59	10.32	139	1.37	1.37	1.37
10.81	10.64	139	0.94	0.90	0.73
10.98	10.75	139	0.94	0.90	0.81

\*222.9 mg of surfactant was used.

## Removal of TNT Using Hexadecylethyldimethylammonium Bromide

One-liter solutions containing varying amounts of hexadecylethyldimethylammonium bromide (Eastman Kodak Company) were prepared. The pH of each was adjusted with NaOH or HCl to  $10.5 \pm 0.5$ . The solutions were stirred at room temperature. Samples were taken periodically, filtered, and the TNT content in each filtrate was determined. The results are summarized in table 6. There was no precipitate when 50 mg of surfactant were used.

Table 6. Removal of TNT using hexadecylethyldimethylammonium bromide

Surfactant used (mg)	Initial pH	TNT left in solution (mg/L)			
		Initial	3 hrs.	4 hrs.	5 hrs.
100	10.59	139	19.1	11.1	8.6
150 <sup>a</sup>	10.35	139	6.8	4.7	4.1
150	10.30	139	6.4	5.1	4.7
150	10.52	139	4.1	4.1	4.1
150	10.65	139	3.7	3.5	3.0
150	10.89	139	4.1	4.0	3.8
200	10.31	139	4.71	3.85	3.70

<sup>a</sup>The molar ratio of surfactant to TNT was 0.85:1

## Removal of RDX and TNT and Radioactive RDX from Aqueous Solution

Thirty-five milligrams of the <sup>14</sup>C tagged RDX were dissolved in 5 mL of pure acetone. The solution was diluted with water to 1 L. This solution was mixed with 1 L of aqueous TNT solution (TNT concentration 130 ppm).

Experiments were carried out on the removal of RDX

from the above solution using 4-dodecyldiethylenetriamine. Two RDX and TNT solutions (750 cc) containing 4-dodecyldiethylenetriamine (molar ratio of TNT:surfactant were 1:3 and 1:4, respectively) were prepared. The solutions were stirred for 50 hours at ambient temperature. The brown precipitate was filtered off and the filtrate (2 mL) was dissolved in 15 mL of Aquasol counting solution. The radioactivity was determined by the liquid scintillation counter and the results are shown in table 7.

Table 7. Removal of RDX from aqueous solution  
(counts minute)

<u>Sample</u>	<u>Before Treatment</u>	<u>After Treatment</u>	
		<u>with surfactant 1:3 molar ratio</u>	<u>with surfactant 1:4 molar ratio</u>
I	375	350	360
II	390	380	360
TNT	65 mg/L	1 mg/L	0.4 mg/L

These data indicate that either the RDX was not removed by these treatments or the decomposed products of RDX have the same radioactivity as the original RDX.

#### Experiments to Remove RDX from Pink Water

The pink water supplied by ARRADCOM (February 3, 1977) was analyzed. It contained TNT at 118 ppm and RDX at 74 ppm. Experiments to remove the RDX and TNT from the pink water were conducted using 4-dodecyldiethylenetriamine. Two 1-L solutions containing the surfactant (mole ratio TNT:surfactant 1:4 and 1:5 respectively) were prepared. The solutions were stirred for 40 hours at ambient temperature. The brown precipitate was filtered off and the concentrations of RDX and TNT were determined. The typical results are shown in table 8.



Table 8. Removal of RDX and TNT from pink water

	<u>Before Treatment</u>	<u>After Treatment</u>	
		<u>with surfactant 1:4 mole ratio</u>	<u>with surfactant 1:5 mole ratio</u>
TNT	118	1 mg/L	1 mg/L
RDX	74	65	65

These data show that the RDX could not be removed by the treatment.

#### Removal of RDX at High Temperature from Pink Water

The rate of reaction of TNT with surfactant increases as the temperature increases (Ref 1). Therefore, experiments were carried out on the removal of RDX and TNT from pink water at high temperature. One-liter solutions of RDX and TNT in varying strengths containing 500 mg of surfactant were prepared. The solutions were heated in a constant temperature bath at 80°C for 12 hours. The brown precipitate was filtered off and the concentration of RDX and TNT were determined. The typical results are shown in table 9.

Table 9. Removal of RDX and TNT at 80°C

	<u>Initial Concentration (mg/L)</u>	<u>After Treatment (mg/L)</u>	
		<u>with N-COCO- surfactant</u>	<u>with N-Tallow- surfactant</u>
TNT	150	0.6	1.5
RDX	76	57	53

These results show that RDX is not effectively removed from pink water even at high temperature by this treatment.

#### Removal of RDX by Strongly Basic Ion Exchange Resins

Non-aromatic, nitroso- or nitro-substituted explosive



compounds can be decomposed by strongly basic anion exchange resins (Ref 2). To evaluate this process for removing RDX from waste water, experiments were carried out using a Dowex-1 anion exchanger. Fifty grams of resin were packed in a 2-in. diameter glass column with 4.5-in. bed length. The resin was in the  $\text{Cl}^-$  form and the anionic ion was regenerated with  $\text{OH}^-$ . The resulting  $\text{OH}^-$  resin was washed twice with deionized water. Five hundred mL of RDX solution (21 ppm) were passed through the column. Samples were collected at 50 mL intervals. The flow rate was 10 mL/min. The samples were analyzed for RDX; the concentration of RDX was less than 1.0 ppm., i.e., 0.2 ppm.

#### Combination Treatment of Surfactant and Ion Exchange Resin

Experiments were carried out to remove RDX and TNT from the pink water using a surfactant and the anionic exchange resin. One-liter solutions containing varying amounts of the surfactants were prepared. The solutions were stirred for 20 hours at ambient temperature. The brown precipitate was filtered off and the concentrations of RDX and TNT were determined. Each filtrate (500 mL) was passed through the ion exchange resin column at a flow rate of 10 mL/min. The concentrations of RDX and TNT in the solutions were analyzed. The results are shown in table 10.

Table 10. Removal of RDX and TNT using surfactant treatment followed by ion exchange

<u>Surfactant</u>	<u>Initial Concentration (mg/L)</u>	<u>Final Concentration (mg/L)</u>					
		<u>After surfactant</u>		<u>After exchanger</u>			
	<u>Surfactant</u>	<u>RDX</u>	<u>TNT</u>	<u>RDX</u>	<u>TNT</u>	<u>RDX</u>	<u>TNT</u>
N-tallow bis-(aminopropyl) amine	290	76	150	57	35.1	0.2	0.0
	290	76	150	61	30.4	0.3	0.6
N-coco-propylene diamine	500	76	150	46	0.6	2.1	0.0
	300	76	150	49	20.6	0.3	0.0

## Removal of RDX by Using the Micellar Effect

Since RDX can be decomposed with  $\text{OH}^-$ , the micellar effect on the rate of decomposition of RDX with  $\text{OH}^-$  in the presence of surfactant was investigated. Solutions (500 mL) containing varying amounts of NaOH with and without the surfactant (ethylhexadecyldimethylammonium bromide) were prepared. The solutions were mixed well and allowed to stand overnight at ambient temperature. Duplicate samples of each solution were analyzed. The results are shown in table 11.

Table 11. Hydrolysis of RDX

<u>Initial Concentration</u>			<u>RDX Concentration after treatment</u> <u>(mg/L)</u>
<u>RDX</u> <u>(mg/L)</u>	<u>Surfactant</u> <u>(M)</u>	<u>NaOH</u> <u>(M)</u>	
21	$10^{-3}$	$10^{-3}$	1.6
21	$10^{-4}$	$10^{-4}$	6.3
21	-	$10^{-3}$	19.4
21	-	$10^{-4}$	19.7

## Removal of RDX and TNT with NaOH and Surfactant

Experiments were carried out on the removal of RDX and TNT from the pink water using the surfactant and varying amounts of NaOH. One-liter solutions containing 300 mg of the surfactant (ethylhexadecyldimethylammonium bromide) and varying amounts of NaOH were prepared. The solutions were stirred for 20 hours at ambient temperature. The suspension was first filtered using filter paper with a filtration aid. In the second filtration, a 0.45 micro-filtration paper was used under pressure of .14 kPa (20 psig.). The typical results are shown in table 12. The concentration of surfactant in Run 4 after treatment was 52 ppm.

Table 12. Removal of RDX and TNT with NaOH and surfactant<sup>a</sup>

Run No.	Initial Concentration <sup>b</sup>			Concentration after treatment (mg/L)		
	NaOH (M)	RDX (mg/L)	TNT (mg/L)	TNT	RDX	
1	$5 \times 10^{-4}$	76	150	6.5	25.5	
2	$1 \times 10^{-3}$	76	150	10.5	16.0	
3	$1.5 \times 10^{-3}$	76	150	2.1	7.5	
4 (c)	$2.0 \times 10^{-3}$	76	150	2.0	10.0	
5	$2.0 \times 10^{-3}$	76	150	1.0	11.5	
6 (c)	$4.0 \times 10^{-3}$	76	150	1.2	0	
7	$4.0 \times 10^{-3}$	76	150	1.0	0	
8 (c)	$5.0 \times 10^{-3}$	76	150	1.3	0	
9	$5.0 \times 10^{-3}$	76	150	1.3	0	

(a) Concentration of surfactant was 300 mg/L

(b) The concentrations of RDX, 76 mg/L, TNT 150 mg/L and surfactant 300 mg/L correspond to  $3.4 \times 10^{-4}M$ ,  $6.6 \times 10^{-4}M$  and  $7.9 \times 10^{-4}M$ , respectively.

(c) Filtered using only filter paper with filtration aid.

Removal of RDX and TNT from Pink Water with NaOH  
and N-Tallow Trimethylammonium Chloride

To develop an economical process for removing RDX and TNT from pink water, a commercial surfactant, N-tallow trimethylammonium chloride<sup>1</sup> was tested. The results are summarized in tables 13 and 14.

Table 13. Effect of treatment time  
on the removal of RDX and TNT at 20°C<sup>a</sup>

<u>Run No.</u>	<u>Time (hr.)</u>	<u>Concentration after Treatment</u> <u>(mg/L)</u>	
		<u>RDX</u>	<u>TNT</u>
1	0	76	150
2	1	75	50
3	2	75	20
4	3	74	7
5	4	72	2.7

<sup>a</sup>The initial concentration of surfactant was  
 $5.75 \times 10^{-4}$  M; pH 11.7

<sup>1</sup> The surfactant was obtained from Ashland Chemical Co. and the trade name is ADOGEN. The price (50% solid) was \$0.57/lb FOB Wisconsin (confirmed on November 17, 1977).

Table 14. Effect of Temperature on  
the removal of RDX and TNT

Run No.	Temperature (°C)	Initial Concentration of Surfactant (M)	Concentration after 4 hrs. Treatment mg/L <sup>a</sup>	
			RDX	TNT
1	20	$3.84 \times 10^{-4}$	70	3.5
2	45	$3.84 \times 10^{-4}$	20.5	3.3
3	60	$3.84 \times 10^{-4}$	1.5	1.5
11	20	$5.75 \times 10^{-4}$	27	2.7
12	45	$5.75 \times 10^{-4}$	20.5	2.0
13	60	$5.75 \times 10^{-4}$	1.3	0.9

<sup>a</sup>Initial concentrations of RDX and TNT were 76 mg/L ( $3.4 \times 10^{-4}$  M) and 150 mg/L ( $6.6 \times 10^{-4}$  M), respectively ; pH 11.7.

The dark brown solids precipitated from TNT solution with surfactants were dried under vacuum. They could burn without explosion. The impact sensitivities of these solids were examined at ARRADCOM, Dover, New Jersey and they were found to be non-explosive. The test results are given in Figure 1. The thermal analysis of these solids are shown in Figures 2 and 3. The data also show that these solids were decomposed without explosion with heating and yielded char (beyond 450°C).

#### Removal of Nitroguanidine from Aqueous Solution Using NaOH and Surfactant

Experiments were carried out to remove nitroguanidine from aqueous solution using ethylhexadecyldimethylammonium bromide (EHDABr). Three solutions containing nitroguanidine and varying amounts of surfactant and NaOH were prepared. The solutions were stirred at ambient temperature, and aliquots were withdrawn periodically to determine their nitroguanidine contents. The results are shown in table 15.

The results indicated that nitroguanidine could not be removed by this process.

AFPA 1000		GOVERN. NEW JERSEY 07000		DATE
REPORT FROM THE <u>ENERGETIC MATERIALS DIVISION - Chem Branch</u>				13 Mar 78
KIND OF SAMPLE	TNT Complexes	REPORT NO.	FMD MI 8-78	
RECEIVED FROM	MSTD, MTD, Mr. M. Roth, Bldg. 3305	DATE RECEIVED	22 Feb 78	
REFERENCE OF X. O.	7833-25-002 (CF2)			
REPRESENTING	Two (2) samples of TNT Complexes Dried in Oven at 75 <sup>+</sup> 5° For 4 hours before testing			
and designated as follows:				
1. N- Tallow propylene diamine - TNT Complex (appeared wet even after drying)				
2. N- Tallow trimethyl ammonium chloride - TNT Complex (dry and free flowing)				
Sample No.	2 Kg PA Impact Sensitivity Test	Results (height, inches)		
1	Charge weight: 0.018 gms	40+		
2	Charge weight: 0.006 gms	40+		
Sample No.	5 Second Decomposition Temperature Test °C			
1	346			
2	366			
Procedure:	Technical Report 3278 Rev 1 except that the sample was tested without performing the granulation specified.			
WORK BY: <u>W. Huff &amp; J. Dippman</u>	SUBMITTED: <u>J.J. Campisi</u>	APPROVED: <u>[Signature] J.C. Castorina</u>		
SAFPA Form 1243 Feb 74				

Figure 1 - Test results

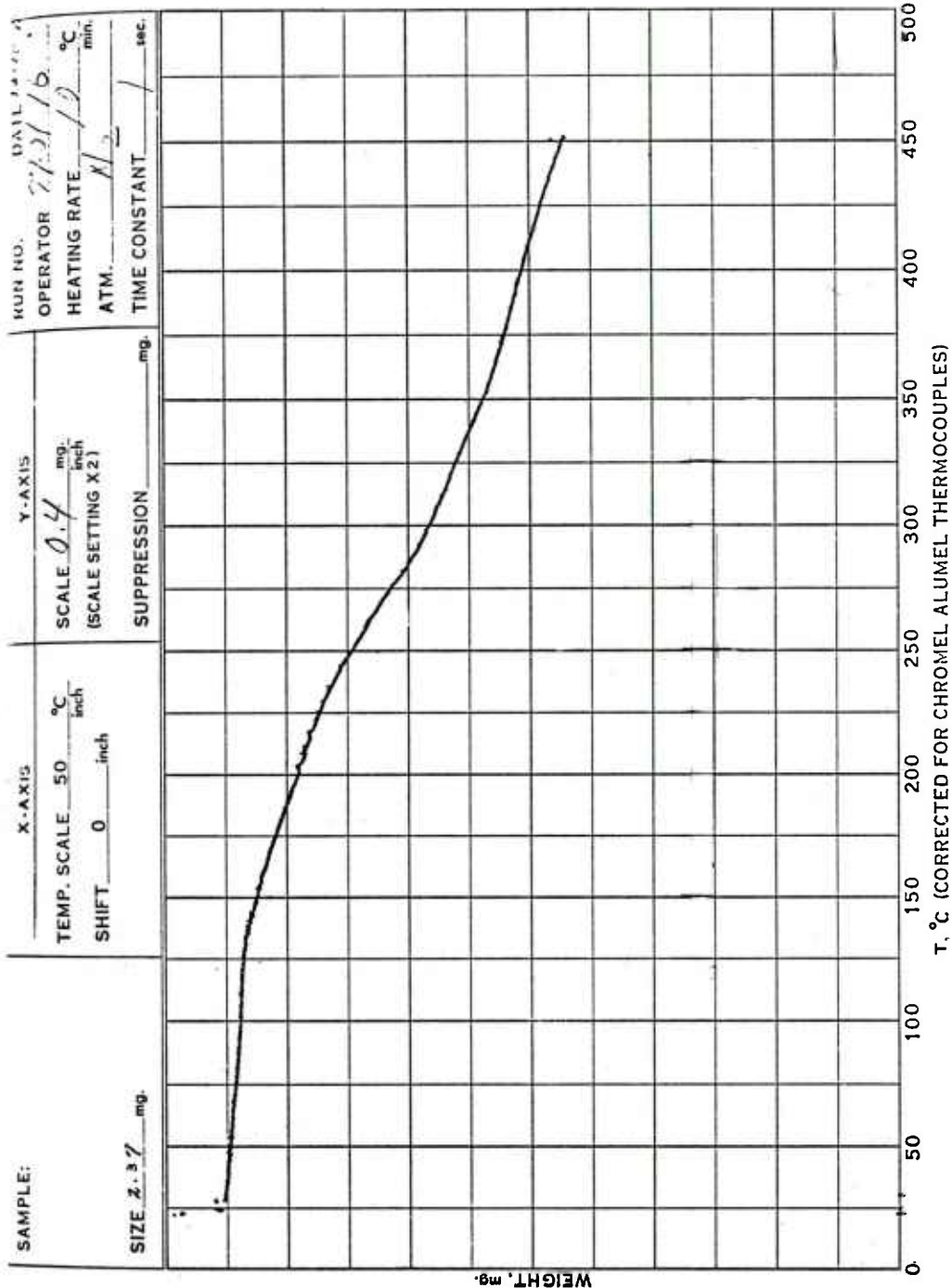


Figure 2 - N-tallow-propylene diamine TNT complex



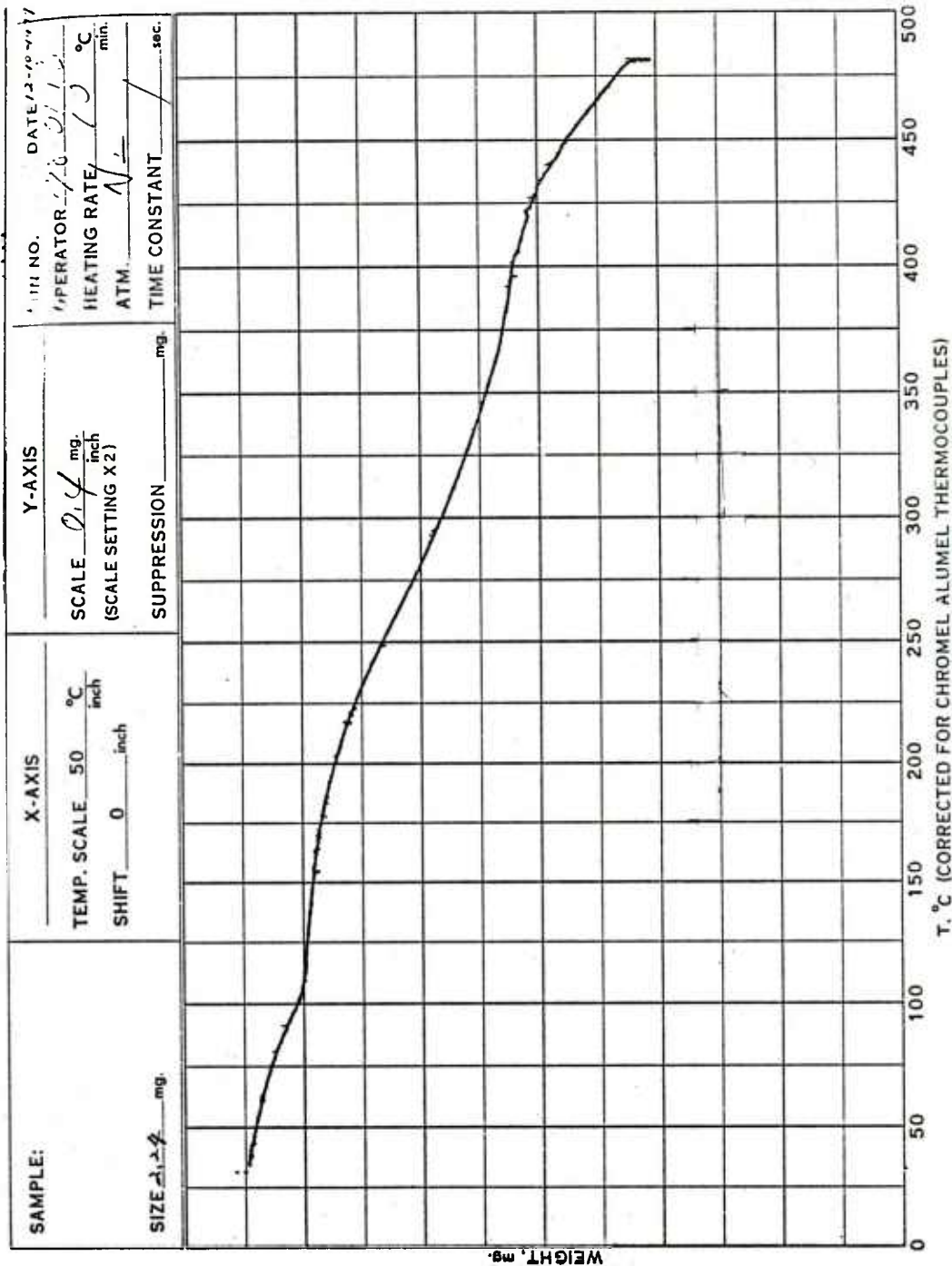


Figure 3 - N-tallow-trimethylammonium chloride  
TNT complex



Table 15. Removal of nitroguanidine  
from aqueous solution

Sample	Initial Concentration		
	Nitroguanidine (mg/L)	EHDABr (mg/L)	NaOH (M)
I	50	200	0
II	50	200	0.005
III	50	0	0.005

Sample	Final Concentration (mg/L)			
	1 hr.	3 hrs.	5 hrs.	24 hrs.
I	50	50	50	50
II	49.8	49.8	49.0	41.8
III	50	49.7	49.4	41.8

#### Removal of Nitroguanidine from Aqueous Solution Using Ion Exchange Resin

Because nitroguanidine is very soluble in water and the hydrolysis of nitroguanidine is not enhanced using the surfactant-NaOH system, we attempted an alternate method for the hydrolysis of nitroguanidine by using a strongly basic ion exchange resin. A typical experiment follows.

About 150 of Dowex 1-X8 anion exchange resin (50/100 mesh) were packed into a nominal 1.5 in. column approximately 24 in. long. The resin bed was 125 mm (5 in.) long. The resin was first treated with 500 mL of 0.1 M NaOH solution and then washed with 500 mL deionized water. Two liters of nitroguanidine (100 mg/L) solution were passed through the ion exchange resin column at room temperature (22°C) at the flow rate of 10 mL/min. Samples were taken periodically and the concentration of nitroguanidine was determined by the absorbance at 265 nm. The results showed that the effluent solution contained less than 1 ppm

of nitroguanidine.

The detailed analysis of the composition of the effluent was not attempted. It was reported in the literature (Ref 3) that nitroguanidine was decomposed with 2 M NaOH at 60° into N<sub>2</sub>O, CO<sub>2</sub> and NH<sub>3</sub>. Thus it was expected that nitroguanidine would decompose into these compounds and sodium salts with the ion exchange resin.

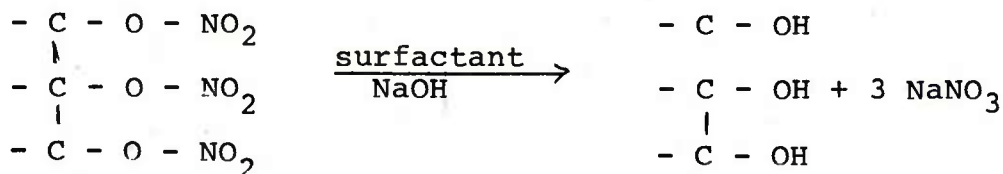
#### Removal of Nitroglycerin from Aqueous Solution using NaOH and Surfactant

Experiments were carried out on the decomposition of nitroglycerin from aqueous solution using a surfactant NaOH system in which solutions containing nitroglycerin, varying amounts of surfactant (ethylhexadecyldimethylammonium bromide (EHDABr)) and NaOH were stirred at ambient temperature. Aliquots were withdrawn periodically and the amounts of nitroglycerin were determined as described above. The results are summarized in table 16.

Table 16. Removal of nitroglycerin from aqueous solution

Run	Initial Concentration			Removal			
	Nitroglycerin (mg/L)	NaOH (M)	EHDABr (M)	3 hrs	4 hrs	18 hrs	24 hrs
1	250	-	-	0	0	0	0
2	250	0.01	$6.75 \times 10^{-3}$	32	46	86	98
3	250	0.01	-	12	20	42	60
4	250	-	$6.75 \times 10^{-3}$	0	0	0	0

The results indicate that the hydrolysis of nitroglycerin was greatly enhanced with surfactant-NaOH system. The products were glycerine and NaNO<sub>3</sub>.



## MATERIALS

Pure RDX was synthesized by the process reported in reference 4. The melting point (mp) of the recrystallized compound was 203-205°C (Ref 4 203-204°C). The infrared spectrum of the compound was identical to that of the pure RDX supplied by ARRADCOM.

<sup>14</sup>C Labelled RDX - To determine RDX concentrations in aqueous solution, <sup>14</sup>C labelled RDX was synthesized from radioactive paraformaldehyde using the procedure in reference 5.

TNT - 2,4,6-Trinitrotoluene was obtained from the Fisher Scientific Company and purified by recrystallization from ethyl alcohol.

HMX - Pure HMX was supplied by ARRADCOM.

Nitroguanidine - Nitroguanidine containing 25% water was obtained from the Aldrich Chemical Company, Incorporated, and purified by recrystallization from ethyl alcohol. The melting point (decomposed) was found to be 239°C.

Nitroglycerin - Nitroglycerin was synthesized by the nitration of glycerin with H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> mixture. The melting point was 13°C (reference 6, 13°C).

Surfactants - Commercially available surfactants were used in this investigation:

N-Cocoa Propylene and N-oleylpropylene diamines were obtained from both General Mills Chemicals, Incorporated, and the Industrial Chemicals Division of Arma.

4-Dodecyldiethylenetriamine and Ethylhexadecyldimethylammonium bromide were obtained from Eastman Kodak Company.

N-Tallow trimethylammonium chloride (Trade name ADOGEN 471) was obtained from Ashland Chemicals.

Hyamine 3500 (dimethylbenzylammonium chloride) was obtained from the Rohm and Haas Company. Its toxicity is described in a Rohm and Haas Co. Technical Bulletin as follows:

Subacute oral toxicity has been found in albino rats fed Hyamine 3500, in concentrations up to 0.25%, for three months. There was no significant effect on mortality, weight gain, or feed consumption. No gross pathological changes were observed at autopsy except for gaseous distension of the cecum. This reaction is characteristic of feeding high levels of quaternary ammonium compounds. The blood picture was normal.

The acute toxicity of Hyamine 3500 has been determined on several species of animals when administered by various routes. The following table gives the LD<sub>50</sub> of Hyamine 3500 active ingredient in milligrams per kilogram of body weight.

Route	Animal	LD <sub>50</sub> mg/kg
Oral	Albino rats	447 $\pm$ 10
Oral	Albino rabbits	496 $\pm$ 70
Oral	Dogs	about 500
Intravenous	Albino rats	31 $\pm$ 2.4

## ANALYTICAL PROCEDURES

### Analysis of RDX and TNT in Pink Water

Several different analytical methods were used to determine the presence of RDX and TNT.

#### Spectrophotometric Analysis of RDX in the Presence of TNT

A procedure for determining the presence of TNT in pink water was developed by Tennessee Eastman Company (Ref 7). Both TNT and RDX absorb light at the same wavelength after treatment, but the presence of TNT can be determined independently by the Mudri process (Ref 8). This process uses a spectrophotometric technique in which the interfering absorbance in a two-component system is eliminated when one of the compounds is determined by an independent method and the absorbance of that is subtracted from the total.

#### Analysis of RDX in Aqueous Solution

1. Transfer 5 mL of the sample solution to a 25 mL volumetric flask.
2. Add 0.5 mL of 0.5 N sodium hydroxide to the flask.
3. Heat the flask in a boiling water bath for 5 minutes.
4. Cool the solution to room temperature.
5. Add 1 mL of color reagent (equal amounts of 0.8% sulfanilamide in 5 N acetic acid and 1% dimethyl  $\alpha$ -naphthylamine in 5 N acetic acid).
6. Allow the solution to stand for 15 minutes and make to volume with distilled water.
7. Read the solution's absorbance at 530 nm using a 10-mm cell.

#### Preparation of the Standard Curves

Both TNT and RDX reaction products absorb light at 530 nm. Therefore, standard curves were prepared for both

TNT and RDX using the procedure for analysis of RDX in aqueous solution as described. The plots of the absorbance versus the concentration of RDX and of TNT were straight lines (Figures 4 and 5 respectively).

#### Analysis of TNT in Aqueous Solution

Mudri (Ref 8) has developed a simple procedure to determine the concentration of TNT in waste water using  $\text{Na}_2\text{SO}_3$  and NaOH. This procedure has been described in reference 1.

#### Calculations

The amount of TNT is obtained by using the Mudri method, and this amount is then used to obtain the absorbance at 530 nm from the standard curve for TNT. When this absorbance is subtracted from the total absorbance of the sample at 530 nm, the corrected absorbance can be used to determine the amount of RDX by the use of the standard curve for RDX.

#### Analysis of RDX in the Presence of Surfactant

It is well known that micellar systems have a considerable effect on indicator equilibrium. To overcome this effect when determining the presence of RDX and TNT using the method described above, an excess of surfactant was added after the solution was heated with NaOH. The absorption maximum ( $\lambda_{\text{max}}$ ) of the solution shifted from 530 nm to 465 nm. The effect of surfactant concentration on the shifting of  $\lambda_{\text{max}}$  is shown in figure 6. The standard curves of RDX and TNT are shown in figures 7 and 8. These corrected absorbances can be used to determine the amount of RDX and TNT when the surfactant is present.

#### High Performance Liquid Chromatographic (HPLC) Method: Normal Phase and Reverse Phase

To avoid the interference of surfactant, the HPLC method was mainly used in this investigation.

#### Preparation of the Standard Curve for RDX

According to reference 9, the equilibrium partition coefficient for RDX between benzene and water is 8.2. Therefore, when a 2:1 ratio (volume) of benzene to water

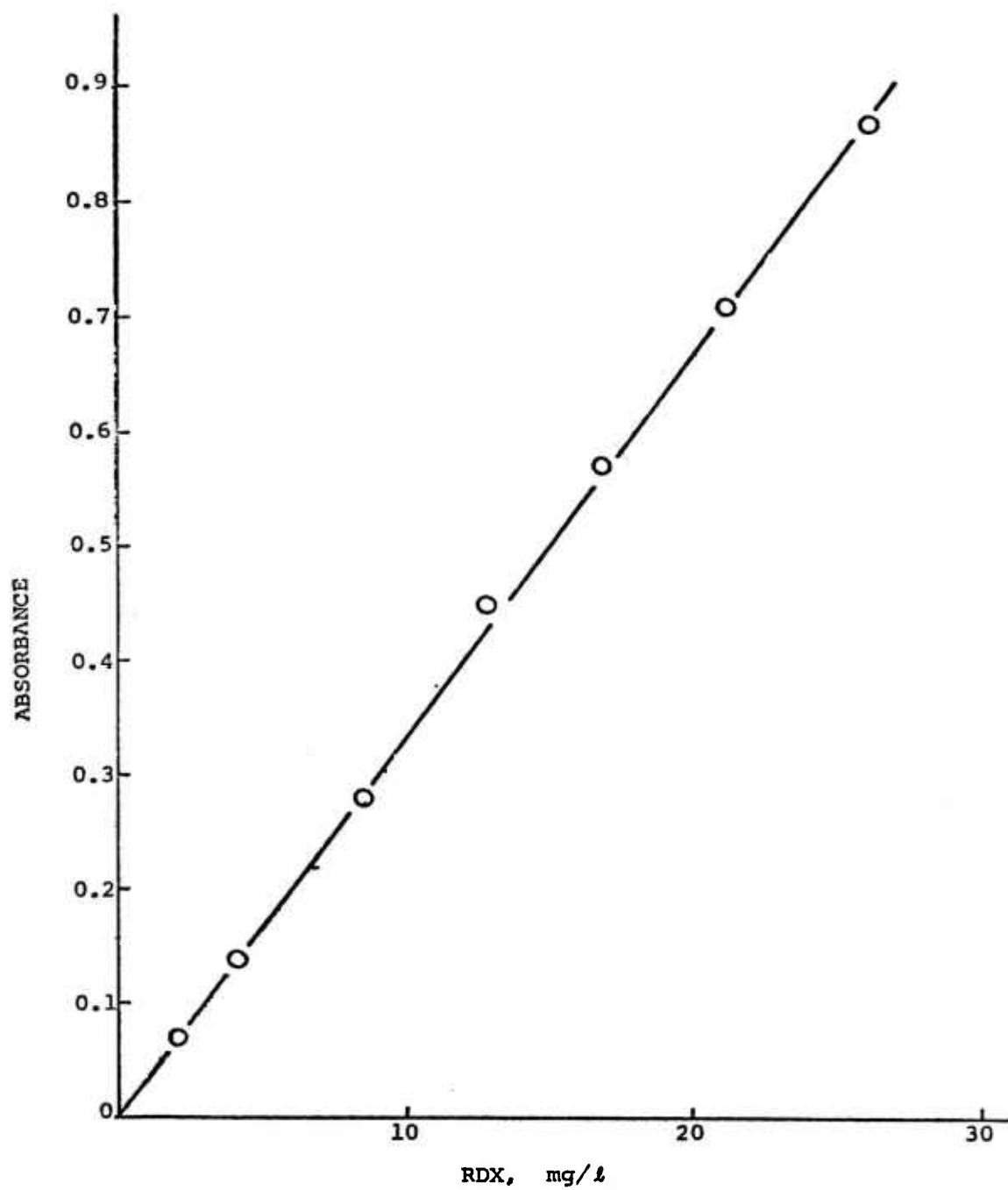


Figure 4 - Calibration curve for determination of RDX of 530 nm.



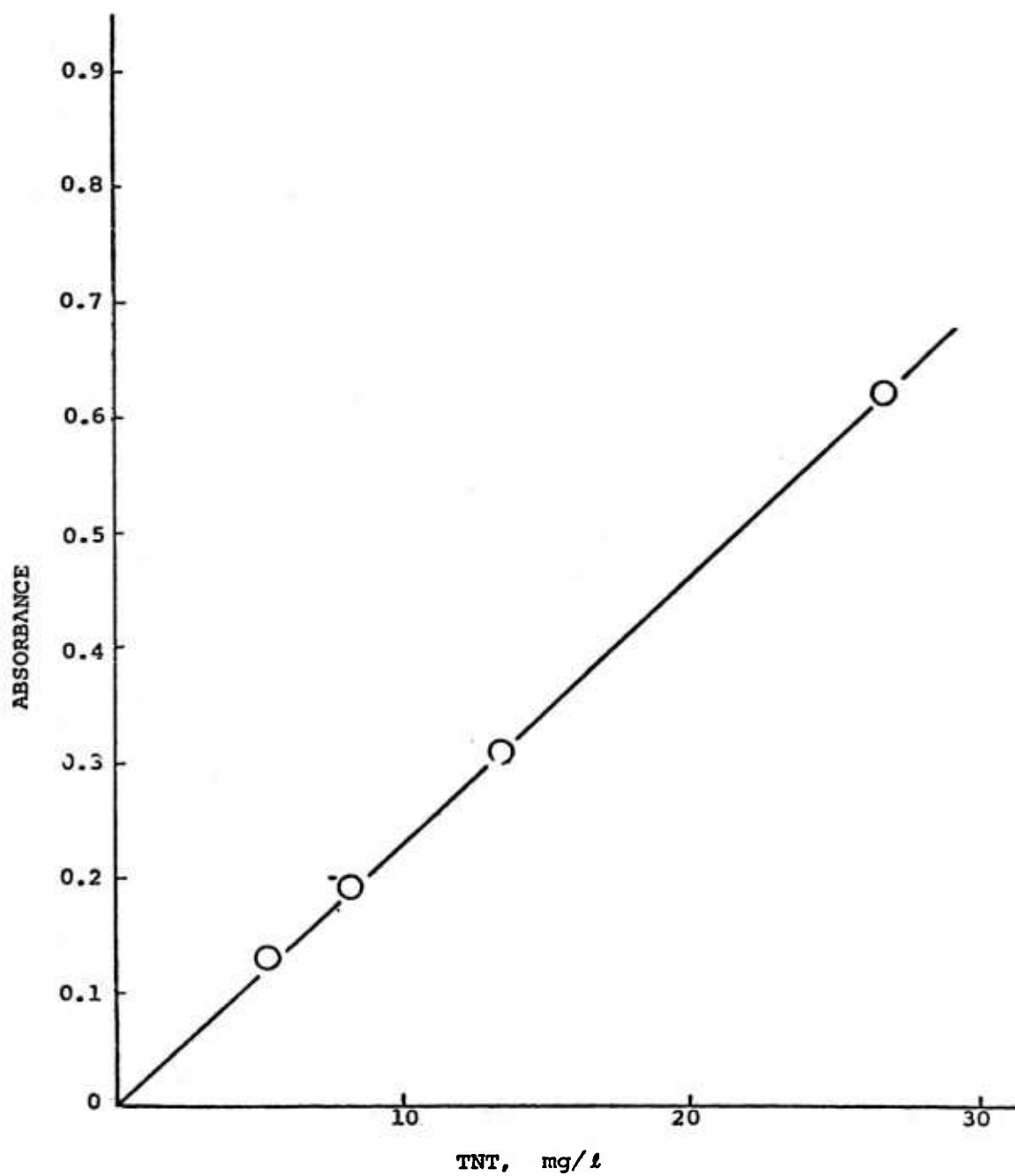


Figure 5 - Calibration curve for determination of TNT at 530 nm.



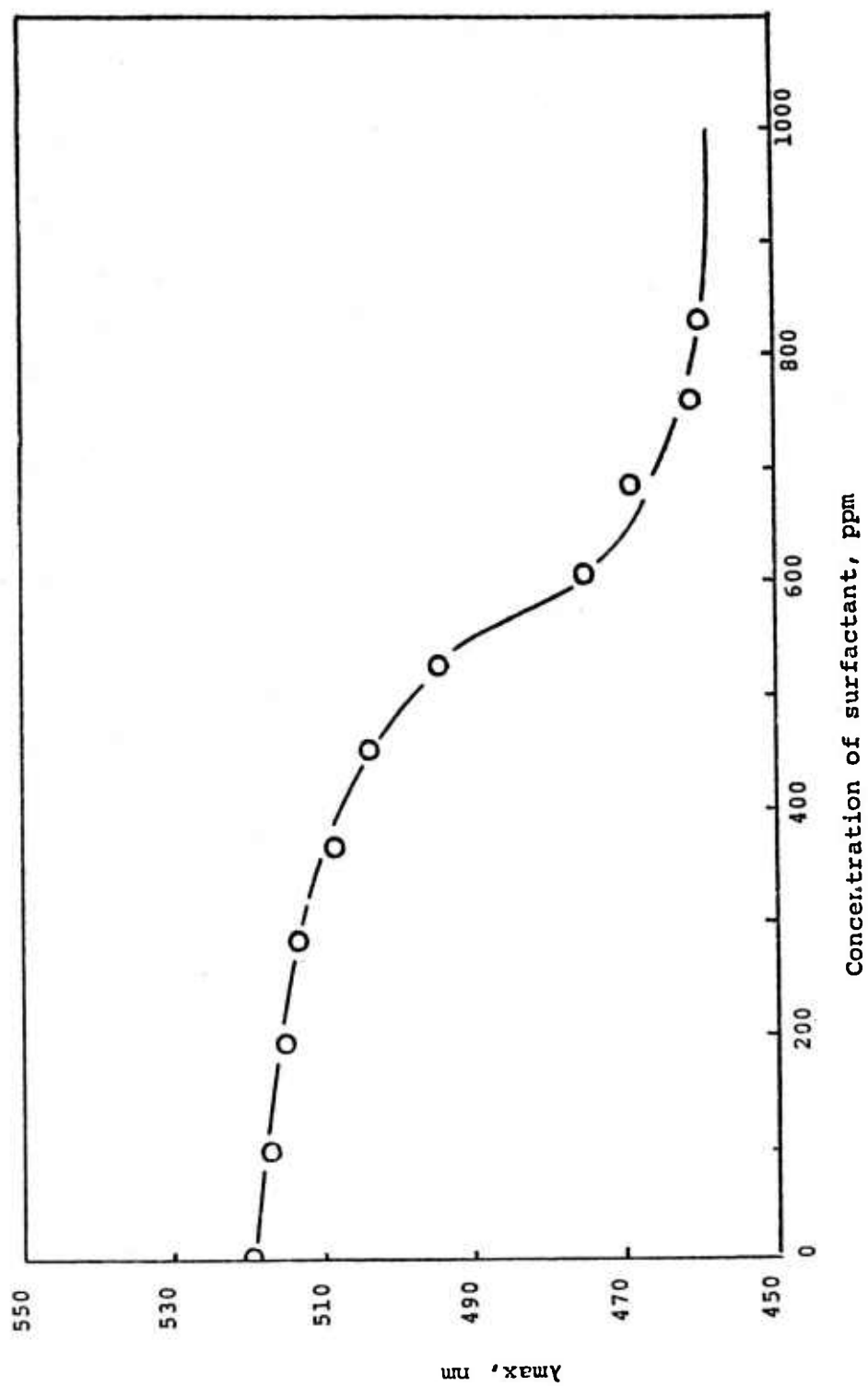


Figure 6 - Surfactant effect on  $\lambda_{\text{max}}$  shifting on determination of RDX.

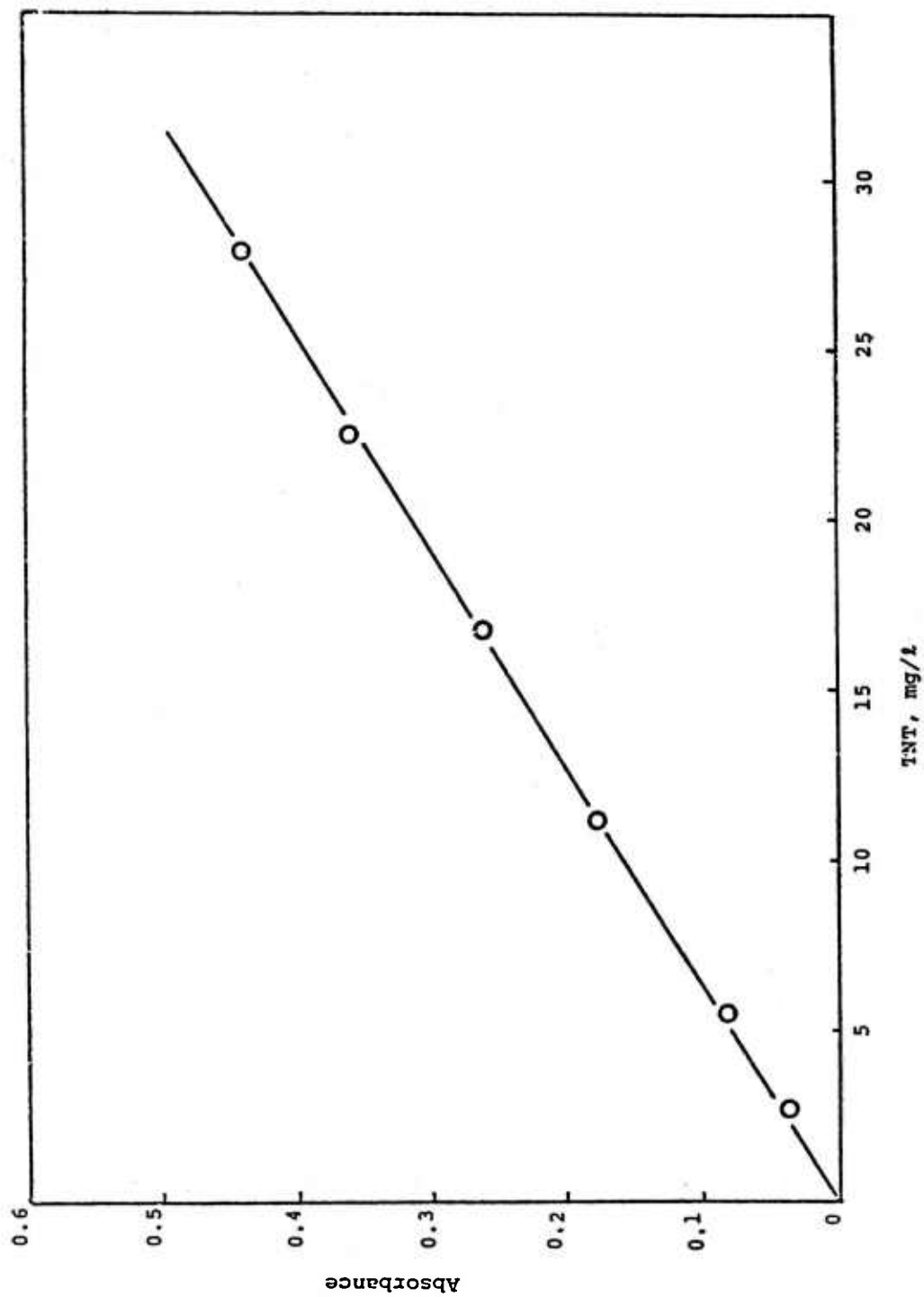


Figure 7 - Calibration curve for determination of TNT at 460 nm .

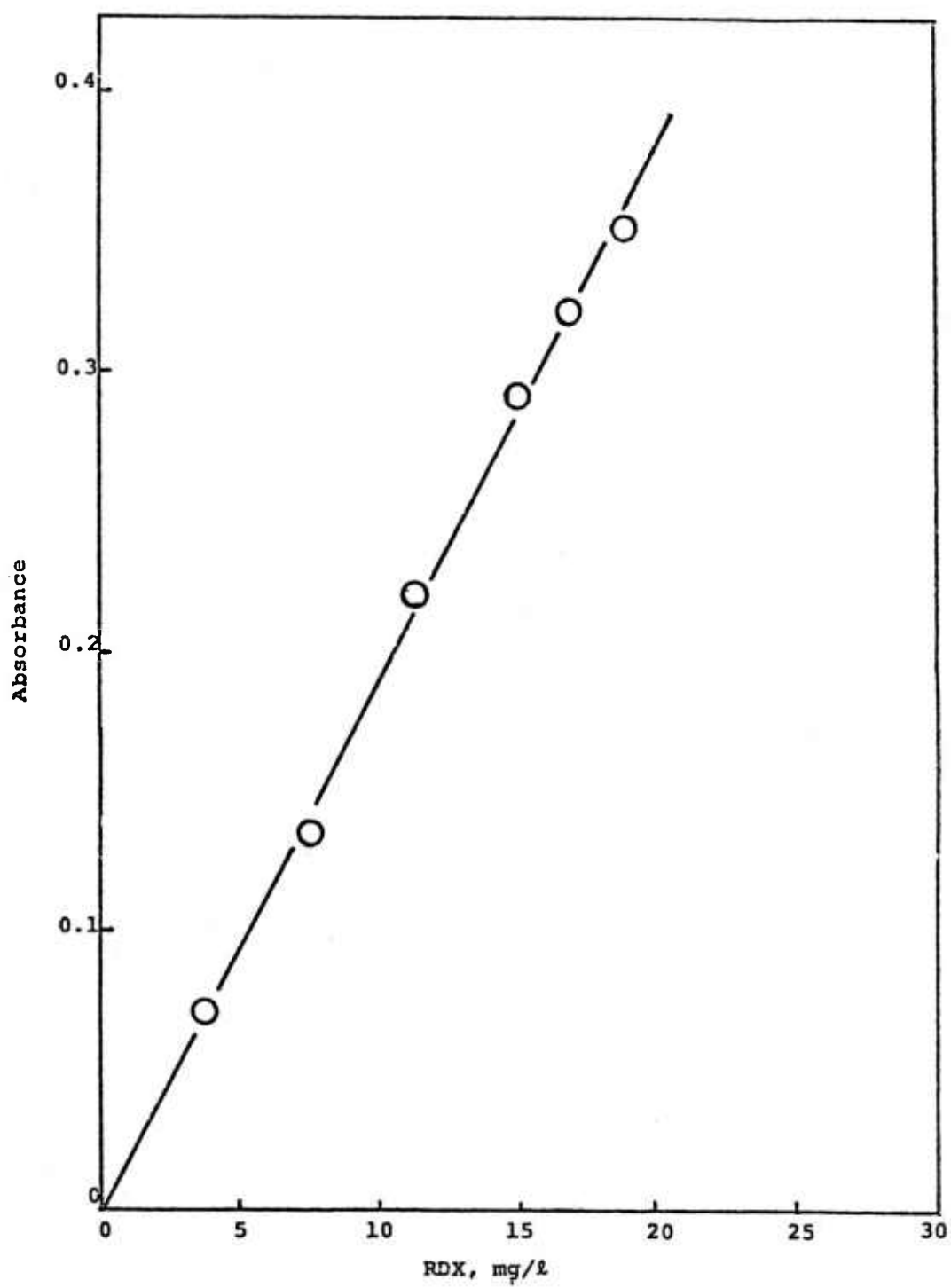


Figure 8 - Calibration curve for determination of RDX at 460 nm .

is used, more than 94% of the RDX can be extracted into the benzene phase. This fact was used to establish the standard curve for RDX. The procedure follows.

Standard aqueous solutions of RDX are prepared by appropriate dilution of a stock RDX solution (20 ppm is suitable). Each dilution is then extracted (2:1 ratio, benzene:RDX aqueous standard). Five-milligram aliquots were taken from each aqueous RDX standard and pipetted directly into 60-mL separatory funnels containing 10 mL of pre-distilled Baker analyzed benzene which had been precisely pipetted into the separatory funnel. The resulting immiscible phases were shaken vigorously for about 20 seconds, allowed to stand for distinct phase separation, and the bottom aqueous layer was discarded. The upper benzene layer was pre-filtered through Whatman #1 filter paper and collected in 25-mL Erlenmeyer flasks. Each standard was filtered using a 0.2 micrometer Teflon Filter obtained from Millipore Corporation, (Boston, Mass.), by using a 5-cc syringe and millipore adapter apparatus. This final filtering was made directly into 2-cc volumetric flasks to the mark.

Fifty microliters of the filtered RDX standard was then injected into a Waters ALC 244 Liquid Chromatograph with the following operating conditions: the UV detector was in operation set at 0.1 AUFS (absorbance units, full scale, calibrated to within  $\pm 0.01$  AU on a Heathkit single pen recorder); the flow rate was 2 mL per minute using tetrahydrofuran as the mobile eluting solvent; the gel permeating columns in use were the 100 and 500 Angstrom micro-Styragel (a porous styrenedivinylbenzene copolymer obtained from Waters Associates).

Peak heights are correlated to peak absorbance values versus concentration in ppm of original RDX aqueous standard. A digital UV readout can be used quite effectively to assure proper calibration throughout the entire analysis. The digital UV readout is part of the Waters ALC 244. The calibration curve for RDX is shown in figure 9.

#### Preparation of the Standard Curve for TNT

A standard TNT curve was prepared in a manner similar to the preparation of the RDX curve. The only modification was the UV detector sensitivity setting: 0.5 AUFS was chosen for TNT-extracted standards. Since the Waters UV de-

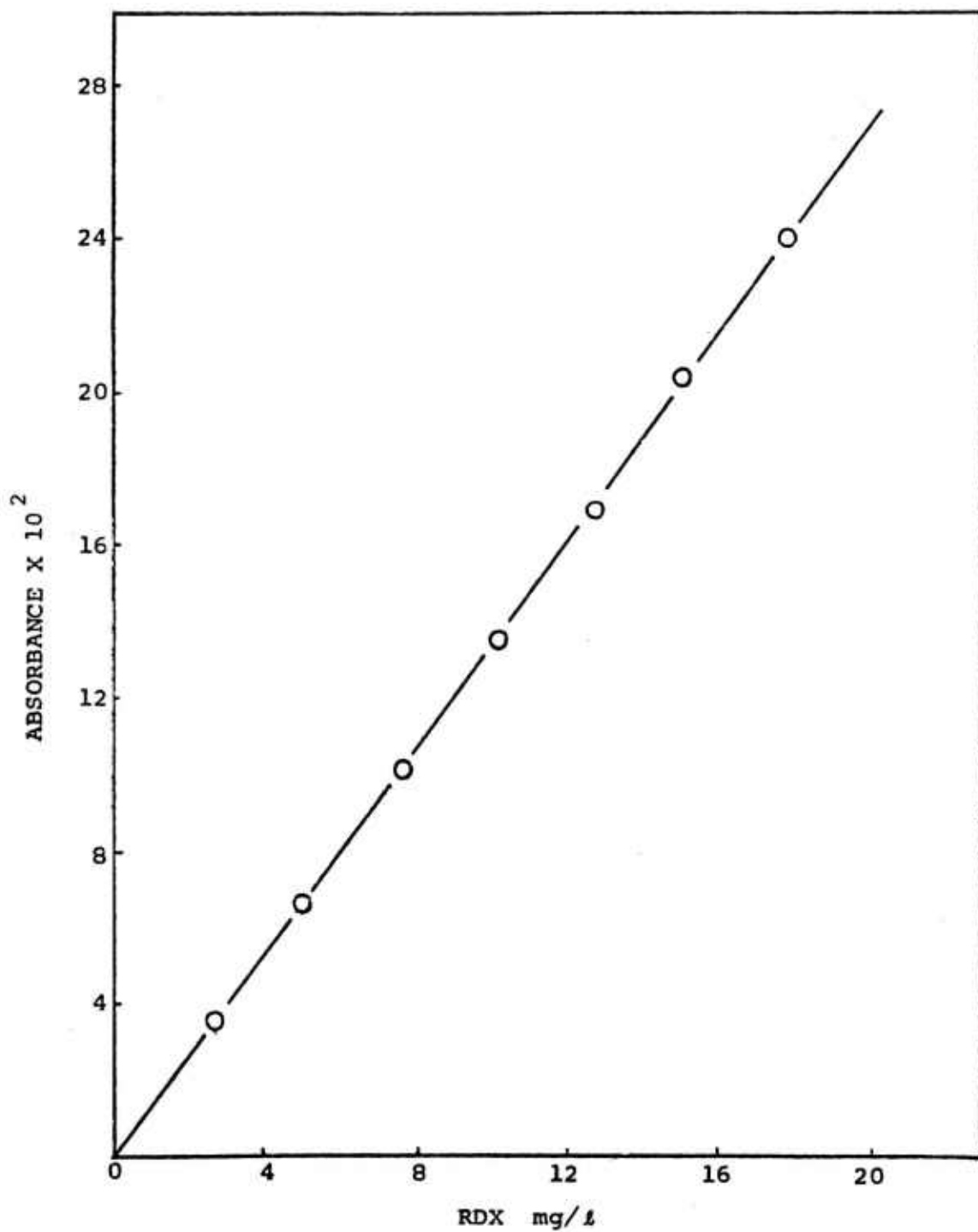


Figure 9 - Calibration curve for RDX using HPLC .

tector is fixed at 254 nm, high absorbance values were expected for TNT because of its aromatic ring structure. The Waters UV monitor is capable of the following sensitivity settings, which lends it great versatility in quantitative operations: 2.0, 1.0, 0.5, 0.2, 0.1, 0.05, 0.005 AUFS. The calibration curve for TNT is shown in figure 10.

#### Reverse Liquid Chromatographic Analysis of Organic Explosives

In a continuing effort by this laboratory to determine the quantities of organic explosives in wastewater precisely and quickly, a reverse phase liquid chromatographic (RPLC) system was employed. In RPLC, a relatively polar mobile phase is used in conjunction with a highly non-polar stationary phase to separate slightly soluble organic trace components. To separate organic explosives, a C-18 Bondapack/Corasil column was obtained from Waters Associates. In essence, the Bondapack column consists of a monolayer of a C-18 hydrocarbon chemically bonded to a silica gel coating on porous glass beads. The bond is a Si-C<sub>18</sub> functionality. This represents the nonpolar phase.

The mobile phases were mixtures of methanol and water. By varying the mobile phases and flow rates and pressures, the organic explosives were separated with adequate resolution.

This system was a distinct advantage over previous normal phase liquid chromatographic systems. The first normal phase liquid chromatographic method used gel permeation columns (micro Styragel, 100 and 500 Angstroms in series) with THF as the mobile eluting phase. Benzene extractions of the explosives and subsequent injections into the HPLC gave an adequate analysis.

The second normal phase method used a Corasil I column (containing a polar stationary phase, silica beads) and a mobile phase consisting of cyclohexane and methylene chloride. Methylene chloride was used to extract the explosives. Considerable time and chemicals were saved by switching to the reverse phase system.

In general, the following conditions were employed in the RPLC analysis of aqueous explosive waste water effluents: Waters ALC-244 High Performance Liquid Chromatograph using the Waters Model 440 UV absorbance detector

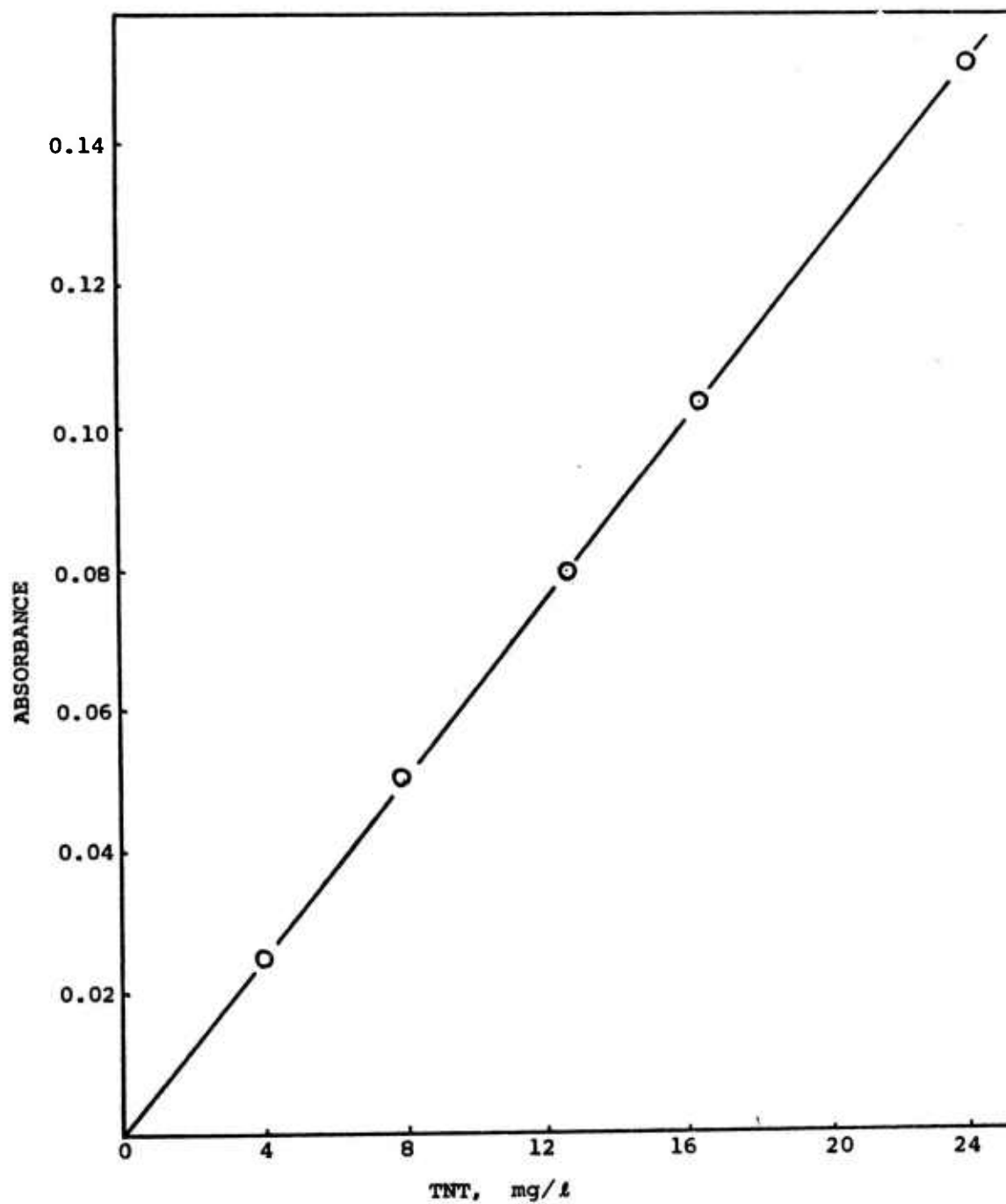


Figure 10 - Calibration curve for TNT using HPLC.



set at an appropriate sensitivity (ranging from 0.005 absorbance units full scale, AUFS to 0.2 AUFS) depending on the level of organic explosives present; mobile phase consisting of a 60:40 mixture of  $H_2O:CH_3OH$ ; flow rate at 1.2 ml per minute with a pressure reading of 750 psi; 50-75 microliter injections were used.

Analysis of explosive wastewater effluent was initiated by running standards at known concentration on the following explosives: RDX, HMX, and TNT. All explosives were recrystallized at least two times from an appropriate solvent system to assure their purity. Melting points and HPLC chromatograms proved them to be quite pure. These standards were then injected into the liquid chromatograph under precisely the same conditions to be employed for the analyses of effluent waste water. A calibration curve was prepared for each of the three organic explosives of interest: RDX, HMX, and TNT. All standards were filtered using a 0.45 micron Millipore apparatus to assure that no solid particulate matter remained which would cause flow and pressure problems with the liquid chromatograph.

Explosive wastewater (both treated and untreated) was filtered using the Millipore apparatus and injected into the liquid chromatograph (LC) under identical conditions of mobile phase composition, flow rate/pressure and UV sensitivity setting. Peak heights were used to calculate concentrations both in the calibration of the standard curves for RDX, HMX and TNT and in the explosive wastewater effluent. In general, only the UV sensitivity setting needed to be changed during the course of analysis in order to bring the various explosive peaks on scale. Retention times of RDX and TNT were adequate so that their concentration could be determined precisely. Retention times using the above LC conditions were: RDX, 120 seconds, and TNT, 170 seconds using a Heathkit recorder at 0.8 inches per minute. Unfortunately, the decomposition products of RDX (generally formaldehyde) overlapped with the HMX peak, so no analysis of HMX could be performed. However, RDX decomposition products did not interfere with any subsequent analysis of TNT or RDX.

#### Determination of Nitroguanidine in Aqueous Solution

Nitroguanidine is determined directly on a diluted sample by ultraviolet spectroscopy. The stock solution was prepared by dissolving 1.000 g dry nitroguanidine in



one liter of distilled water. Standard solutions were prepared by diluting the stock solution to the desired concentrations and the nitroguanidine concentration measured by the absorbance of each solution at 267 nm using a 1 cm cell. The  $\lambda_{\text{max}}$  is not affected by the presence of a surfactant (ethylhexadecyldimethylammonium bromide). The absorbance verses the concentration of nitroguanidine was found to follow Beer's Law, as shown in figure 11.

#### Determination of Nitroglycerin

The concentration of the nitroglycerin in water was determined by using a Waters Associates liquid chromatograph. The typical procedure of the analysis follows.

Nitroglycerin was extracted from the aqueous solution with methylene chloride (2:1 water to methylene chloride volume ratio). Since the analysis can be impaired by colloidal particles, the methylene chloride solution was filtered first through a Whatman #1 filter paper and then through a 0.2 micrometer Teflon filter. The final filtrate was injected into the chromatograph. The UV detector was used with the flow rate set at 1.0 mL/minute using methylene chloride as the mobile phase. The column was Corasil I (Waters Associates) which contained a solid core glass bead with a silica gel layer and particle range of 37 to 50 micrometers.

#### Calibration Curve for Nitroglycerin Determination

Standard aqueous solutions were prepared by appropriate dilution of a stock nitroglycerin solution (1000 mg/L). Each standard dilution was then extracted with methylene chloride, treated as described in the previous section, and injected into the HPLC. The relationship between UV absorbance and the amount of nitroglycerin was found to be a linear relationship, and the result is shown in figure 12.

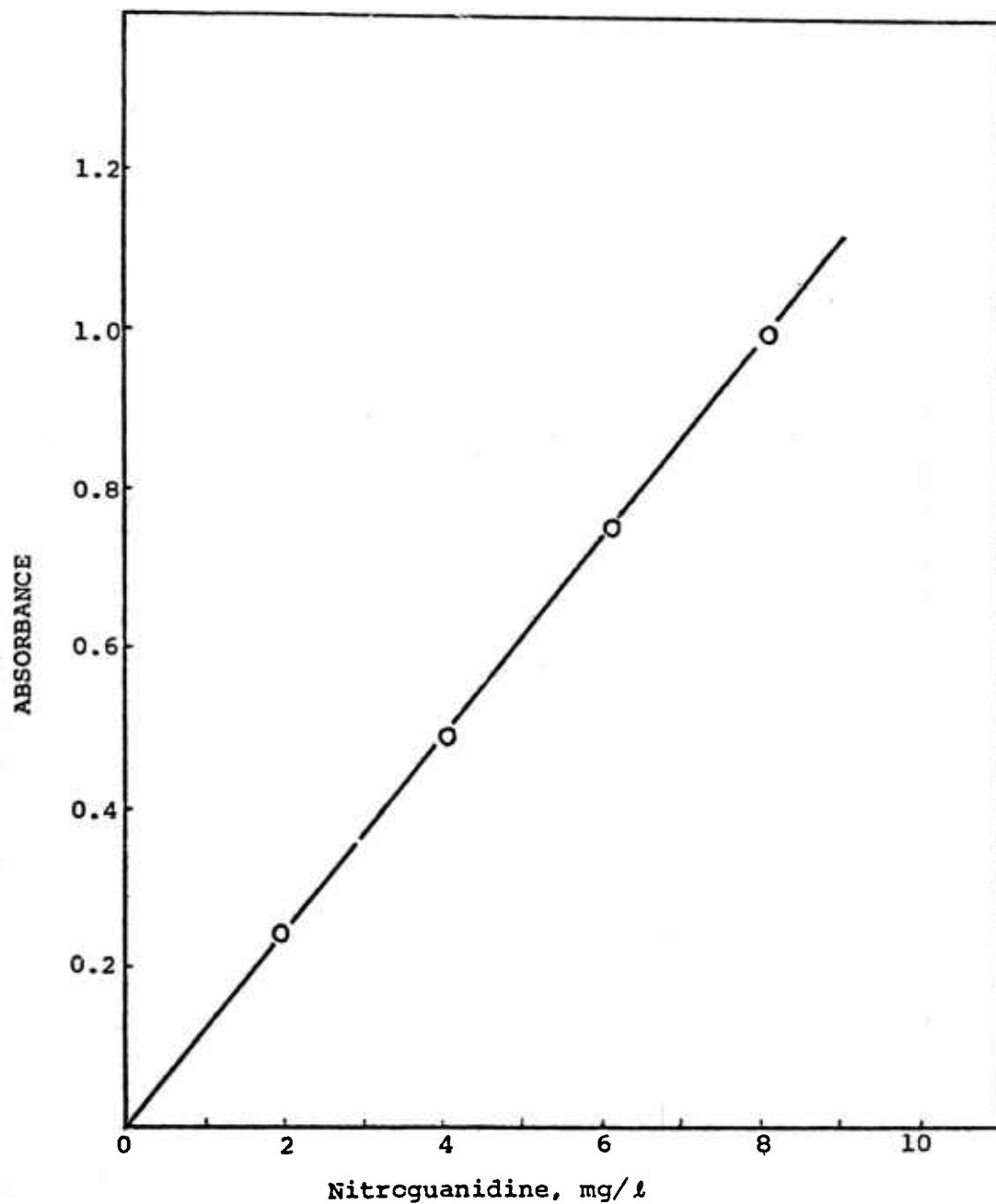


Figure 11 - Calibration curve for determination of nitroguanidine at 267 nm using 1 cm cell.

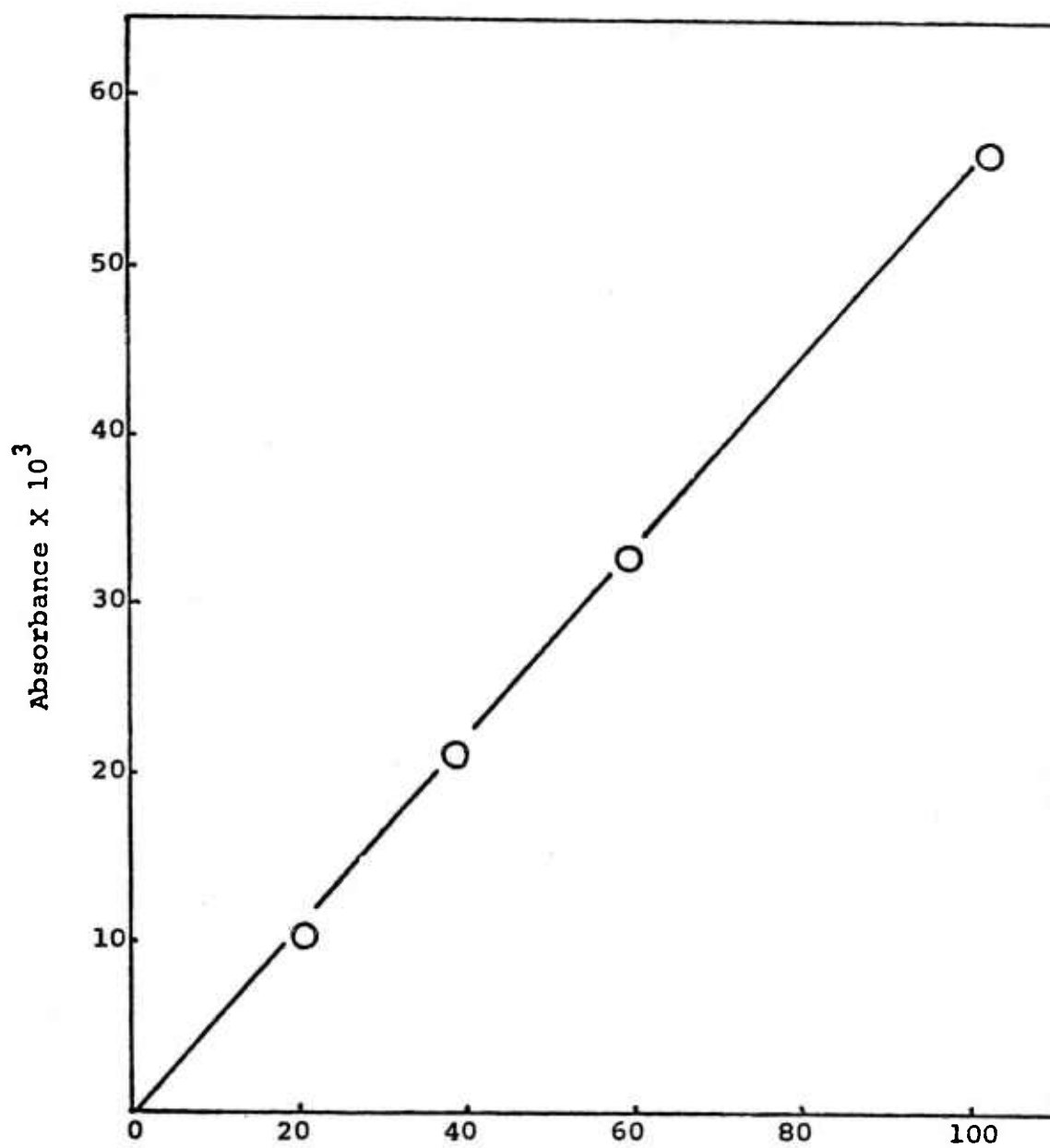


Figure 12 - Calibration curve for nitroglycerin using HPLC with uv detector .

## ECONOMIC EVALUATION

The major expense in the process for the treatment of pink water is the cost of N-tallow trimethylammonium chloride, one of the most effective surfactants that could be used. This surfactant is available from Ashland Chemical Company under the trade name ADOGEN 471. The efficiency of the simultaneous removal of TNT and RDX (decomposition) from pink water is dependent on the pH, temperature, concentration and reaction time. As shown in table 14, the optimum conditions are as follows:

pH	11.5 $\pm$ 0.5
Concentration of Surfactant	0.75 to equal molar of TNT concentration
Temperature	about 60°C
Reaction time	4 hours

The cost calculation based on the above optimum condition is listed below:

### 1. Cost of Surfactant

- a. Based on 600,000 gal pink water containing TNT at 150 ppm (750 lbs. TNT) and RDX at 76 ppm.
- b. Based on \$0.57/lb. (50% solid) Ashland Chemicals, FOB Wisconsin, Nov. 17, 1977.
- c. Based on 1 molar ratio of surfactant to TNT.
- d. Molecular weight (average) of surfactant is 340.

### 2. The cost of the surfactant for 1,000 gal. pink water treatment

$$\text{Price surfactant (1 lb.)} \times \text{lb. of TNT in 1,000 gal} \times \frac{\text{MW of surfactant}}{\text{MW of TNT}}$$

$$\$1.14 \times \frac{750}{600} \times \frac{340}{227} = \$2.13$$

### 3. The cost of NaOH

NaOH required for 1,000 gal. treatment is about 700 g.

The cost of 700 g of caustic soda is about \$0.20.

#### 4. Operation Cost

(Discharge of the complex produced and neutralization of waste water with acid, etc.) is estimated as \$.17. Total cost for 1,000 gal. pink water treatment is \$2.50.

This cost may be reduced to \$0.20 when 0.8 mole of the surfactant is used for 1.0 mole of TNT.

The capital investment of this process is minimal. The existing TNT waste water treatment plant can be used with little modification. The operation cost of this process requires a small amount of electricity, steam, maintenance, labor, repairing and instrument maintenance. There are too many contributing factors and too many unknowns to permit quantitative estimates of operating costs.

## DISCUSSION OF PROCESS

The processes for the removal (or decomposition) of organic explosives from aqueous solution using cationic surfactant at high pH are simple and safe.

The TNT reacted with a cationic surfactant such as N-tallow trimethylammonium chloride and NaOH at an initial pH in the range of 10.5-11.5 at ambient temperature. The dark brown particles which separated were removed by filtration. The filtrate contained only a trace amount of TNT ( $< 1$  mg/L).

The precipitate isolated was insoluble in water and non-explosive. Treatment with acid or base, followed with extraction by organic solvent, did not liberate the TNT.

RDX was hydrolyzed quantitatively in aqueous solution with the cationic surfactant at pH  $11.0 \pm 0.5$ .

Nitroglycerin was also hydrolyzed quantitatively with NaOH. The rate of the hydrolysis increased in the presence of the surfactant.

Nitroguanidine was quantitatively decomposed with alkaline solution. The rate did not increase in the presence of the cationic surfactant.

This invention opens a new area of chemistry and the following questions may be asked:

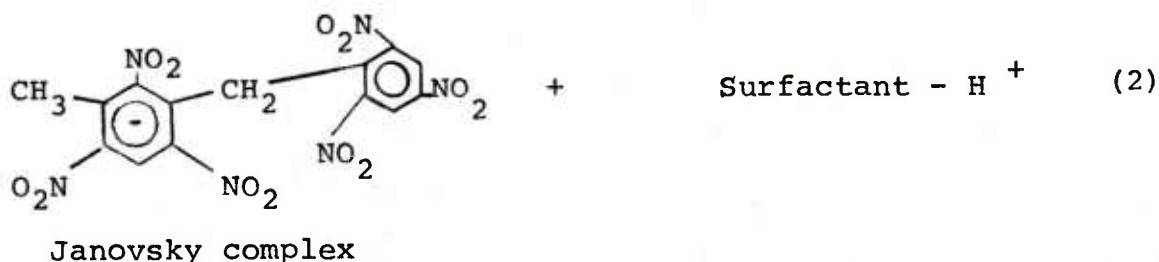
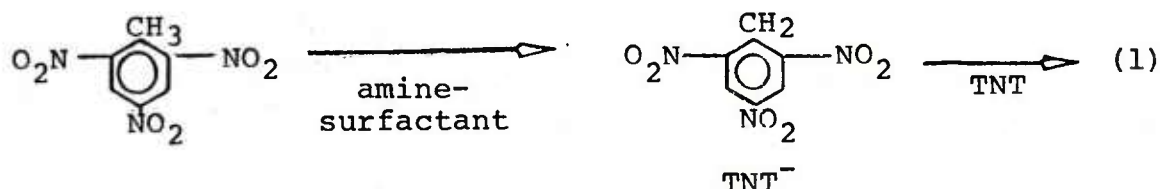
1. What kind of reactions took place between TNT and the cationic surfactant?
2. What are the structures of the precipitates?
3. What is the role of the surfactant?

As we discussed in reference 1, the TNT reacted with amine in aqueous solution to form 2,4,6-trinitrobenzyl anion ( $\text{TNT}^-$ ).

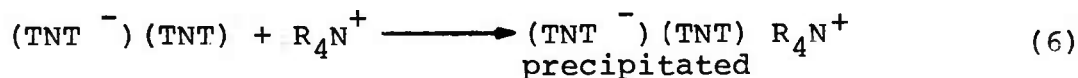
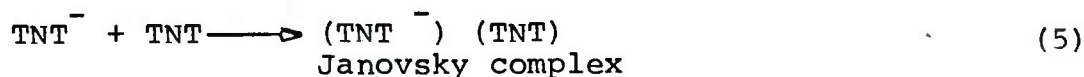
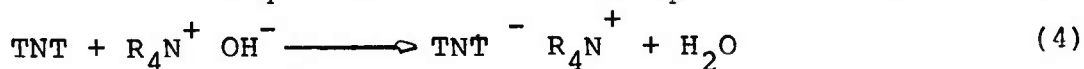
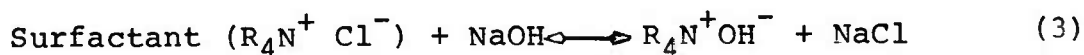
The reaction rate was very slow when simple amines were reacted. However, the rate increased 50 to 150 fold with an amine having a surface active property when the concentration of the amine used was above the critical micelle concentration ( $> 10^{-4}$  M). This increase is ac-

counted for by the micellar effect of the surfactant (references 10 and 11).

The  $\text{TNT}^-$  anion initially produced could react with TNT to form the Janovsky complex. The complex reacted with the protonated surfactant and precipitated as a salt.

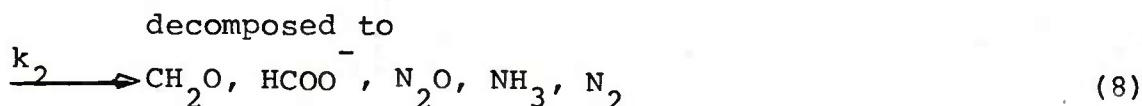
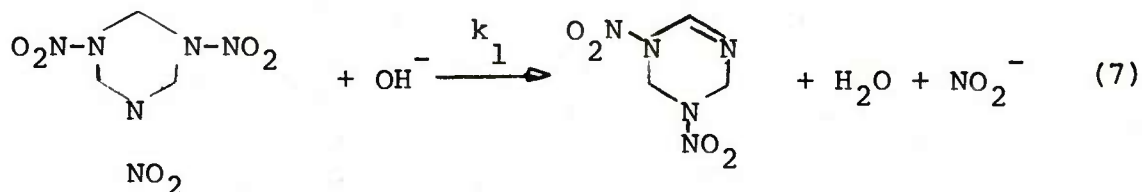


For the reaction of TNT with the cationic surfactant - NaOH system, the complex formations may be illustrated as follows:



The precipitated complex did not decompose to TNT by treatment with acid or base. The rate of the reaction increased greatly (about 200 fold) in the presence of the surfactant over the reaction by NaOH alone. This increase is also accounted for by the micellar effect of the surfactant.

The aqueous alkaline hydrolysis of RDX and HMX has been reported in references 9,12, and 13. The mechanism of the alkaline hydrolysis of RDX was postulated as follows:



$K_1$  is the rate-determining step;  $K_2$  was reported to be  $10^5$  times greater than  $K_1$ .

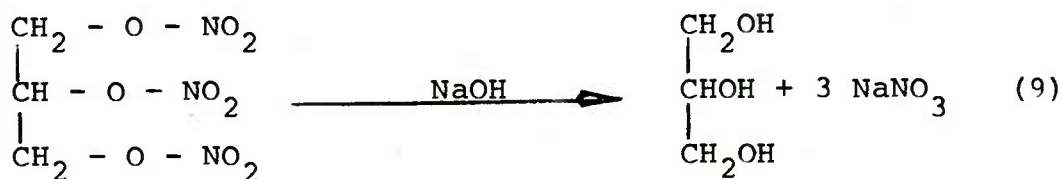
RDX has a limited solubility ( $\sim 70$  ppm) in water at room temperature, and the reaction rate of RDX with NaOH is very slow at ambient temperature. However, we have found that the rate is greatly increased in the presence of a cationic surfactant ( $\sim 75$  fold) (Ref 14). Thus, when the pink water was treated with the cationic surfactant-NaOH system, the TNT was precipitated as the complex,  $(\text{TNT}^-)(\text{TNT})^+\text{surfactant}^+$ . The RDX contained was simultaneously decomposed into  $\text{CH}_2\text{O}$ ,  $\text{HCOO}^-$ ,  $\text{N}_2$ , etc.

The mechanism of the alkaline hydrolysis of HMX has not been reported, but the hydrolysis presumably follows the same course as RDX. HMX was much less soluble in water than RDX. The hydrolysis of HMX with  $\text{OH}^-$  was much slower than that of RDX.

The rate of alkaline hydrolysis of HMX was increased about 25 fold in the presence of a cationic surfactant. Thus, the system can be used for the treatment (decomposition) of waste water containing HMX.

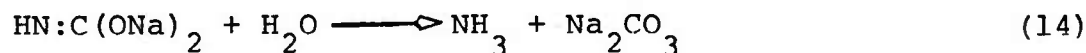
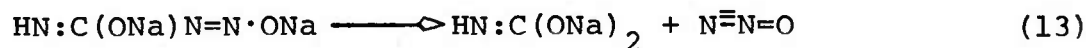
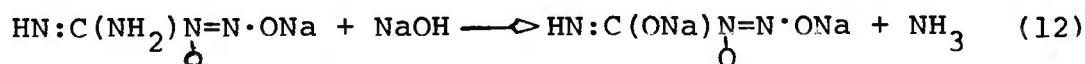
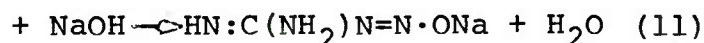
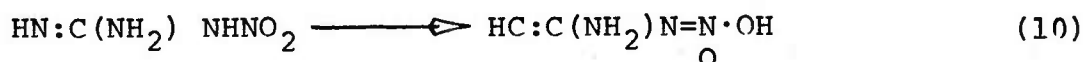
References 15 and 16 report that nitroglycerin can be hydrolyzed in alkaline and acid solutions. The hydrolysis in a neutral solution is extremely slow. The second-order reaction kinetic rates were reported for the hydrolysis with  $\text{OH}^-$  (Ref 17).





The alkaline hydrolysis rate increased in the presence of a cationic surfactant. The increase may also have been caused by the micellar effect of the surfactant.

Numerous references are recorded concerning the reaction of nitroguanidine with caustic alkalies (Ref. 18, 19, 20). Jousselin (Ref. 18) noted the evolution of ammonia. Pellizzari (Ref. 19) observed the formation of sodium carbonate, ammonia and nitrous oxide. The following reaction mechanism for the action of sodium hydroxide upon nitrourea was proposed (Ref. 21).



In the 2 N NaOH solution at 60°C, nitroguanidine was cleaved to  $\text{N}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{NH}_3$  (Ref. 22). Since nitroguanidine is very soluble in water, we did not observe any rate increase in the alkaline hydrolysis of the compound in the presence of a cationic surfactant.

## CONCLUSIONS

1. TNT can be quantitatively removed from aqueous solution with commercial surfactants such as N-tallow trimethyl ammonium chloride and N-tallow propylene diamine by adjusting the initial pH of the solution to 10.5 by NaOH or HCl.
2. TNT and RDX can be simultaneously removed quantitatively from aqueous solution (pink water) with tetra-alkyl ammonium salt surfactants and NaOH at the initial pH in the range of 10.5-11.5 at ambient temperature.
3. The rate of removal (decomposition for RDX) was greatly increased by increasing the reaction temperature.
4. Nitroguanidine can be quantitatively decomposed when the aqueous solution is passed through alkaline anion exchange resin at ambient temperature.
5. Nitroglycerin can be hydrolyzed quantitatively with a surfactant-NaOH system at ambient temperature.
6. The TNT and RDX removal process developed for pink water is simple, safe, and economical. The complex of TNT and surfactant is insoluble in water and not explosive.
7. The major cost for this process is the surfactant used. This cost would be offset by eliminating carbon adsorption but more definitive economic data are required for a complete economic analysis.

## RECOMMENDATIONS

1. The biodegradability of the TNT-surfactant complex should be investigated.
2. The use of the TNT complex should be investigated.
3. The structures of the complex should be further investigated.
4. Consideration should be given to applying these processes to lagoons containing TNT and RDX waste waters and to soils contaminated with explosives.
5. A pilot-scale test for the process of removing TNT and RDX with a surfactant should be carried out.
6. The recommended optimal condition of the process is as follows:

Concentration of surfactant: 0.75 to 1.00 equal molar  
to TNT concentration

Surfactant: N-tallow trimethylammonium chloride

Initial pH:  $11.5 \pm 0.5$

Temperature: about 60°C

Reaction time: 4-5 hours

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